



Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

Evaluation Number 14

NASA Panel for Data Evaluation:

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ABSTRACT

This is the fourteenth in a series of evaluated sets of rate constants and photochemical cross sections compiled by the NASA Panel for Data Evaluation.

The data are used primarily to model stratospheric and upper tropospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena.

Copies of this evaluation are available in electronic form and may be printed from the following Internet URL:

<http://jpldataeval.jpl.nasa.gov/>

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INTRODUCTION

This compilation of kinetic and photochemical data is an update to the 13th evaluation prepared by the NASA Panel for Data Evaluation. The Panel was established in 1977 by the NASA Upper Atmosphere Research Program Office for the purpose of providing a critical tabulation of the latest kinetic and photochemical data for use by modelers in computer simulations of stratospheric chemistry. Table I-1 lists this publication's editions:

Table I-1. Editions of this Publication

	Edition	Reference
1	NASA RP 1010, Chapter 1	(Hudson [1])
2	JPL Publication 79-27	(DeMore et al. [12])
3	NASA RP 1049, Chapter 1	(Hudson and Reed [2])
4	JPL Publication 81-3	(DeMore et al. [10])
5	JPL Publication 82-57	(DeMore et al. [8])
6	JPL Publication 83-62	(DeMore et al. [9])
7	JPL Publication 85-37	(DeMore et al. [3])
8	JPL Publication 87-41	(DeMore et al. [4])
9	JPL Publication 90-1	(DeMore et al. [5])
10	JPL Publication 92-20	(DeMore et al. [6])
11	JPL Publication 94-26	(DeMore et al. [7])
12	JPL Publication 97-4	(DeMore et al. [11])
13	JPL Publication 00-3	(Sander et al. [14])
14	JPL Publication 02-25	(Sander et al. [13])

In addition to the current edition, several of the previous editions are available for download from the website.

Panel members, and their major responsibilities for the current evaluation are listed in Table I-2.

Table I-2. Panel Members and their Major Responsibilities for the Current Evaluation

Panel Members	Responsibility
S. P. Sander, Chairman	Editorial Review, publication, website
M. J. Kurylo V. L. Orkin	OH reactions with halocarbons
D. M. Golden	Three-body reactions, equilibrium constants
R. E. Huie	Aqueous chemistry, thermodynamics
B. J. Finlayson-Pitts C. E. Kolb M. J. Molina	Heterogeneous chemistry
R. R. Friedl A. R. Ravishankara	Upper Troposphere/Lower Stratosphere gas-phase chemistry
G. K. Moortgat	Photochemistry

As shown above, each Panel member concentrates his efforts on a given area or type of data. Nevertheless, the Panel's final recommendations represent a consensus of the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case.

Communications regarding particular reactions may be addressed to the appropriate panel member:

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I.1 Basis of the Recommendations

The recommended rate data and cross sections are based on laboratory measurements. In order to provide recommendations that are as up-to-date as possible, preprints and written private communications are accepted, but only when it is expected that they will appear as published journal articles. Under no circumstances are rate constants adjusted to fit observations of atmospheric concentrations. The Panel considers the question of consistency of data with expectations based on the theory of reaction kinetics, and when a discrepancy appears to exist this fact is pointed out in the accompanying note. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure or temperature dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of important rate constants for which no experimental data are available, the panel may provide estimates of rate constant parameters based on analogy to similar reactions for which data are available.

I.2 Scope of the Evaluation

In the past (releases 1-12 of this evaluation) it has been the practice of the Panel to reevaluate the entire set of reactions with individual Panel members taking responsibility for specific chemical families or processes. In recent years, the upper troposphere and lower stratosphere (UT/LS) have become the primary areas of focus for model calculations and atmospheric measurements related to studies of ozone depletion and climate change. Because the UT/LS is a region of relatively high chemical and dynamical complexity, a different approach has been adopted for future releases of the evaluation. Specifically, the entire reaction set of the data evaluation will no longer be re-evaluated for each release. Instead, specific subsets will be chosen for re-evaluation, with several Panel members working to develop recommendations for a given area. This approach will make it possible to treat each subset in

greater depth, and to expand the scope of the evaluation to new areas. It is the aim of the Panel to consider the entire set of kinetics, photochemical and thermodynamic parameters every three review cycles. Each release of the evaluation will contain not only the new evaluations, but also recommendations for every process that has been considered in the past. In this way, the tables for each release will constitute a complete set of recommendations.

It is recognized that important new laboratory data may be published that lie outside the specific subset chosen for re-evaluation. In order to ensure that these important data receive prompt consideration, each evaluation will also have a “special topics” category. Feedback from the atmospheric modeling community is solicited in the selection of reactions for this category.

For the current evaluation, the specific subsets include the following:

- Hydrocarbon chemistry of the upper troposphere (C3 hydrocarbons and below).
- Reactions of OH and Cl with halocarbon species.
- Photochemistry of halocarbon species.
- Heterogeneous processes on liquid sulfuric acid and soot surfaces
- Thermodynamic parameters (entropy and enthalpy of formation)
- The special topics category includes the following reactions: $O_3 + hv$, $O + O_2 + M$, $OH + O_3$, $HO_2 + O_3$, $OH + NO_2 + M$, $HO_2 + NO_2 + M$, $OH + HNO_3$, $OH + ClO$, $HO_2 + ClO$ and $ClO + ClO + M$.

I.3 Format of the Evaluation

Changes or additions to the tables of data are indicated by shading. A new entry is completely shaded, whereas a changed entry is shaded only where it has changed. In some cases only the note has been changed, in which case the corresponding note number in the table is shaded.

I.4 Computer Access

This document is available online in the form of individual chapters and as a complete document in Adobe PDF (Portable Data File) format. Files may be downloaded from <http://jpldataeval.jpl.nasa.gov/>. This document is not available in printed form from JPL.

Individuals who wish to receive notice when the web page is revised should submit email addresses in the appropriate reply box on the web page.

For more information, contact Stanley Sander (Stanley.Sander@jpl.nasa.gov).

I.5 Data Formats

In Table 1 (Rate Constants for Bimolecular Reactions) the reactions are grouped into the classes O_x , HO_x , NO_x , Organic Compounds, FO_x , ClO_x , BrO_x , IO_x , SO_x and Metal Reactions. The data in Table 2 (Rate Constants for Association Reactions) are presented in the same order as the bimolecular reactions. The presentation of photochemical cross section data follows the same sequence.

I.6 Units

The rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. Thus, for first-, second-, and third-order reactions the units of k are s^{-1} , $cm^3 \text{ molecule}^{-1} s^{-1}$, and $cm^6 \text{ molecule}^{-2} s^{-1}$, respectively. Cross sections are expressed as $cm^2 \text{ molecule}^{-1}$, base e.

I.7 Noteworthy Changes in This Evaluation

I.7.1 Bimolecular Reactions

I.7.1.1 Hydrocarbon Reactions Important in the Upper Troposphere

Atmospheric observations suggest that photochemistry in the upper troposphere has a much greater global significance than previously believed. The production of O_3 in this region is significant and is controlled by interaction of the HO_x and NO_x radical families. Increasingly, it has been recognized that organic compounds (e.g. ketones, aldehydes, peroxides, and acids) play an important role in supplying HO_x to the upper troposphere. NO_x sources in this region are numerous and long-lived reservoir species such as peroxyacyl nitrates (e.g. PAN) and peroxy nitric acid (PNA) serve to redistribute NO_x globally.

In addition, there is renewed interest in the role of convective activity in lifting short-lived hydrocarbons and halocarbon species to levels near the tropopause. If the convection does not directly penetrate the stratosphere, the reactive organics and organo-halogens are likely to react in the upper troposphere. This would be a mechanism for the transport of aldehydes and peroxides noted above. In case of the organo-halogen compounds, releasing degradation products and/or chlorine and bromine radicals in the upper troposphere can be significant. The subsequent fate of the degradation products, especially whether they survive long enough to be transported from the upper troposphere into the stratosphere to affect the halogen budget, is an important open question.

In this update we have considered a set of reactions of importance in upper tropospheric HO_x, NO_x and shortlived halocarbon chemistry. The set includes reactions of OH and Cl with selected alkyl peroxides, organic acids, alkyl and acyl nitrates, aldehydes, and alcohols. It also includes reactions of Cl with various alkylhalides.

We have also updated kinetics parameters for a number of alkylperoxy self- and cross-reactions of importance in upper tropospheric HO_x chemistry. The reactions of peroxy radicals have been studied in the laboratory for many years. However, there are some key difficulties associated with such studies. First, many of the peroxy radicals of interest to the atmosphere are radical-radical reactions that are inherently difficult to study in isolation. For example, many of the reactions of peroxy radicals cannot be carried out under pseudo-first order conditions. Second, many peroxy radical reactions produce reactive products that unavoidably lead to further reactions with the species being monitored. Third, most peroxy radicals do not fluoresce and none have been observed via a fluorescence technique. They also have weak, unstructured absorption spectra in the ultraviolet, which often overlap with those of other peroxy radicals. Therefore, a sensitivity and selectivity method for the detection of peroxy radicals is missing. Lastly, in general, peroxy radical reactions often have more than one set of products.

Previously, it was not always possible to perform a critical analysis using a self-consistent data base because (a) all the information about the experiments was not available, (b) it required re-analysis of previous data in light of new information such as absorption cross sections and product yields, and (c) the knowledge of the interfering reactions and their rates was also uncertain. Therefore, a panel of scientists who have worked with the peroxy radicals of interest to the atmosphere and whose data usually form the basis of recommendations was assembled as a part of the SPARC-IGAC initiative. This panel critically reevaluated the existing data, discarded some, and modified others to arrive at a self-consistent evaluation of the rate coefficients and product yields in the reactions of RO₂ radicals. This effort resulted in a paper that was published in the Journal of Geophysical Research [15]. The current recommendation uses these evaluated data.

Our consideration of upper tropospheric reactions has resulted in the addition of 18 new reactions, most of which involve reactions of Cl with alkyl nitrates, alkyl halides and organic peroxides and acids. Changes to the existing reactions mainly represent small refinements of the Arrhenius parameters and tightening of the uncertainty limits. One significant change involves the OH + acetone reaction rate coefficient which may exhibit curved Arrhenius behavior.

1.7.1.2 OH + Halocarbon Reactions

A comprehensive review of the reactions of industrial and naturally occurring halocarbons with the hydroxyl radical (OH) was conducted for this evaluation. In doing so, attempts were made to understand and reconcile apparent differences between the results of absolute and relative rate measurements for some of the reactions. Relative rate constants were “renormalized” using the revised recommendations for the reference reactions. Thus, the re-evaluation procedure was an iterative one, since relative rate studies themselves were often included as the basis for the rate constant recommendations of these very reference reactions. The recommendations were then checked for self-consistency by seeing whether ratios of the recommended rate constants were in agreement with published relative rate measurements.

In some cases, disparities may seem to exist. However, it should be recognized that the focus of this re-evaluation was the generation of recommended rate constants over the temperature range of atmospheric importance (i.e., below 300 K). Many of the latest (or relatively recent) absolute rate studies have focused on this region but often extend to temperatures greater than 300 K. Relative rate investigations, on the other hand, have been conducted predominantly above room temperature, with only limited extension below 300 K. This can lead to difficulties in evaluating the studies since many of the OH + halocarbon reactions exhibit pronounced Arrhenius curvature. This curvature has several possible causes including multiple reaction pathways (different types of abstractable H atoms), multiple reactant conformers (whose populations and reactivity differ with temperature), and tunneling. Of course, convincing evidence had to exist that such Arrhenius behavior was indeed real and not an artifact of the experimental procedure. For example, one of the common reasons for experimentally observed non-Arrhenius behavior is the

presence of highly reactive impurities in the samples used in the absolute measurements. However, most recent absolute studies have involved thorough reactant sample purification and analysis and curvature in the Arrhenius plot is not likely due to such impurities. Thus, in the presence of real Arrhenius curvature, a rate constant expression derived predominantly from absolute rate constant measurements conducted below room temperature may not be appropriate for normalizing relative rate constant measurements conducted above room temperature. More detail about these issues may be found in the notes for the reactions of OH with HFC-152a and HFC-152 (reactions E7 and E8, respectively).

For some reactions in this section, there have been significant revisions in the recommendations as a result of new and improved studies. For other reactions, only minor changes from earlier recommendations have been made. Nevertheless, in all cases, such changes were made so that the complete set of recommendations is completely current with the published literature and is self-consistent. Finally, several new reactions have been included and the rate constant uncertainty factors (f and g) have been carefully reviewed in an attempt to narrow the range of rate constant uncertainties for modeling purposes. Previous uncertainty limits were overly conservative in some cases. In the present evaluation, the 2σ confidence limits derived from these factors were visually inspected together with the complete experimental database for consistency.

1.7.1.3 Absorption Cross Sections and Quantum Yields

The database for the evaluation of the absorption cross sections and quantum yields has been expanded considerably for all the halocarbon compounds. Whereas the previous evaluation JPL 97-4 reported only the absorption cross sections of a limited number of selected halocarbons, the present evaluation includes now a comprehensive review of most halocarbons of atmospheric relevance investigated in recent years.

The newly evaluated halocarbons are listed in Table 4. This list includes new entries for C₁ to C₄ chloroalkanes, C₁ to C₂ chlorofluoroalkanes (CFCs) and C₁ to C₃ hydrochlorofluorocarbons (HCFCs). For these species the database was expanded from 14 to 26 compounds. Moreover, the database for the brominated hydro- and mixed halocarbons, including halons, was increased from 6 to 18 compounds. Finally, a large range of iodine-containing compounds (total 32) has now been implemented in the present evaluation.

Also new in this section is the incorporation of temperature-dependence data, including the parameters used to express the temperature variation of the absorption cross sections by a polynomial expansion formula. These expressions will allow the calculation of absorption cross sections in a wide range of stratospheric temperatures. Finally, quantum yield data have also been updated for many species.

1.7.2 Heterogeneous Processes

New and/or updated evaluations in this document have focused on uptake measurements on binary liquid sulfuric acid/water solutions, supplemented in a few cases by data on ternary liquid sulfuric acid/nitric acid/water solutions, on water ice, and on "soot" (see definitions in the section on heterogeneous chemistry). No updates on solid acid/ice compositions are presented in this document, although evaluations for key nitrogen oxide sequestration and/or halogen activation reactions on nitric acid trihydrate (NAT) surfaces were recently re-evaluated and presented in JPL 00-3 [14]. Uptake data on alumina, salt and aqueous salt solutions have not been updated since JPL 97-4 [11]. Henry's law solubility data for reactive upper tropospheric/stratospheric species in binary liquid sulfuric acid/water, and, where available, in ternary liquid sulfuric acid/nitric acid/water solutions have also been updated and a much more extensive compilation of Henry's law parameters for pure water has been added.

1.7.3 Thermodynamic Parameters

The table in Appendix 1 contains selected entropy and enthalpy of formation values at 298 K for a number of atmospheric species. As much as possible, the values were taken from primary evaluations, that is, evaluations that develop a recommended value from the original studies. Otherwise, the values were selected from the original literature, which is referenced in the table. Often, the enthalpy of formation and the entropy values are taken from different sources, usually due to a more recent value for the enthalpy of formation. The cited error limits are from the original references and therefore reflect widely varying criteria. Some enthalpy values were corrected slightly to reflect the value of a reference compound selected for this table; these are indicated. Values that are calculated or estimated are also indicated in the table.

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